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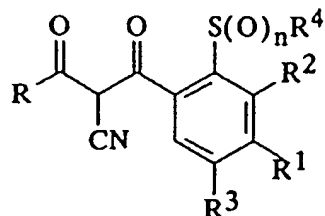
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(54) 2-Cyano-1,3-dione herbicides.

(57) Compounds of formula :



wherein :

R represent an optionally substituted alkyl or an optionally substituted cycloalkyl group ;
R¹ represents halogen, hydrogen, nitro, -O(CH₂)_mOR⁵, cyano, -SR⁵, R⁵, OR⁵, CO₂R⁵ or alkyl
substituted by OR⁵ ;

R² and R³ represent a halogen, hydrogen, R⁵, alkyl substituted by -OR⁵, -O(CH₂)_mOR⁵, nitro, cyano,
-OR⁵ or -CO₂R⁵ ;

R⁴ and R⁵ represent an optionally substituted alkyl group ;

n represents zero, 1 or 2 and

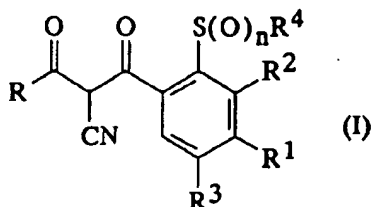
m represents an integer from 1 to 3 ;

and agriculturally acceptable salts of enolic tautomeric forms thereof are useful as herbicides.

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This invention relates to novel 2-cyano-1,3-dione derivatives, processes for their preparation, compositions containing them, and their use as herbicides.

The present invention provides 2-cyano-1,3-diones of general formula I:



15 wherein:

R represents:-

a straight- or branched-chain alkyl group containing up to 6 carbon atoms which is optionally substituted by one or more halogen atoms which may be the same or different; or

a cycloalkyl group containing from 3 to 6 carbon atoms which is optionally substituted by one or more groups selected from R⁵ and one or more halogen atoms which may be the same or different;

20 R¹ represents:-

a halogen atom or hydrogen atom, or

a straight- or branched-chain alkyl group containing up to 6 carbon atoms which is substituted by -OR⁵;

or

25 a group selected from R⁵, nitro, cyano, -SR⁵, -OR⁵, -O(CH₂)_mOR⁵, or -CO₂R⁵;

R² and R³, which may be the same or different, each represents:-

a halogen or hydrogen atom, or

a straight- or branched-chain alkyl group containing up to 6 carbon atoms which is substituted by -OR⁵;

or

30 a group selected from R⁵, nitro, cyano, -OR⁵, -O(CH₂)_mOR⁵, or -CO₂R⁵;

provided that at least one of R² and R³ is hydrogen;

R⁴ and R⁵, which may be the same or different, each represents:-

a straight- or branched-chain alkyl group containing up to 6 carbon atoms which is optionally substituted by one or more halogen atoms which may be the same or different;

35 m is an integer from 1 to 3; and

n is zero, 1 or 2;

with the proviso that when n is zero, R¹ does not represent -SR⁵;

and where the compounds exist in enolic tautomeric forms, agriculturally acceptable salts thereof, which possess valuable herbicidal properties.

40 Compounds of formula I may exist in enolic tautomeric forms that may give rise to geometric isomers around the enolic double bond. Furthermore, in certain cases the substituents R, R¹, R², R³, R⁴, and R⁵ may contribute to optical isomerism and/or stereoisomerism. All such forms are embraced by the present invention.

By the term "agriculturally acceptable salts" is meant salts the cations of which are known and accepted in the art for the formation of salts for agricultural or horticultural use. Preferably the salts are water soluble.

45 Suitable salts formed by compounds of general formula I which are acidic, i.e. in enolic tautomeric forms, with bases include alkali metal (e.g. sodium and potassium) salts, alkaline earth metal (e.g. calcium and magnesium) salts, and ammonium (e.g. diethylmethylamine and morpholine) salts.

The compounds of this invention represent in some aspects of their activity an improvement over known compounds.

50 A preferred class of compounds of formula I (because of their herbicidal properties) are those wherein the substituents have the following preferred meanings:

(a) R represents for example methyl, isopropyl, t-butyl, cyclopropyl or 1-methylcyclopropyl; and/or

(b) R¹ represents:-

a halogen atom or hydrogen atom, or

a group selected from

-OR⁵, for example methoxy, ethoxy or trifluoromethoxy, or

R⁵, for example methyl or trifluoromethyl, or

nitro; and/or

(c) R² and R³, which may be the same or different, each represents:-

a halogen atom or hydrogen atom,

a straight- or branched-chain alkyl group containing up to 6 carbon atoms which is substituted by

-OR⁵, for example methoxymethyl; or

a group selected from

R⁵, for example methyl or trifluoromethyl,

-OR⁵, for example methoxy, ethoxy or isopropoxy,

-O(CH₂)_mOR⁵ where m is 2 or 3, for example 2-ethoxyethoxy or 2-methoxyethoxy,

or -CO₂R⁵, for example carbomethoxy, carboethoxy, or carboisopropoxy,

provided that at least one of R² and R³ represent hydrogen; and/or

(d) R⁴ represents:-

a straight- or branched-chain alkyl group containing up to 4 carbon atoms which is optionally substituted by one or more halogen atoms, which may be the same or different, for example isopropyl, methyl or ethyl; and/or

(e) R⁵ represents:-

a straight- or branched-chain alkyl group containing up to 4 carbon atoms which is optionally substituted by one or more halogen atoms, which may be the same or different for example methyl, ethyl, isopropyl, or trifluoromethyl; and

(f) 'halogen' represents chlorine, bromine or fluorine.

A further preferred class of compounds of general formula I are those in which R³ represents a hydrogen atom.

A further preferred class of compounds of general formula I are those wherein:

R represents isopropyl, cyclopropyl or 1-methylcyclopropyl;

R¹ represents hydrogen, chlorine, bromine, trifluoromethyl, methoxy or methyl;

R² and R³ each represent hydrogen;

R⁴ represents methyl, ethyl or isopropyl; and

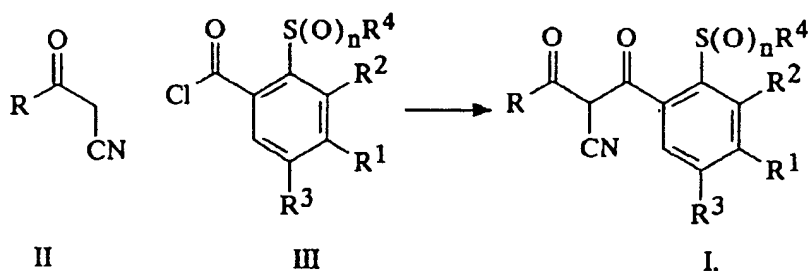
n is zero, 1 or 2.

The compounds of general formula I can be prepared as hereinafter described.

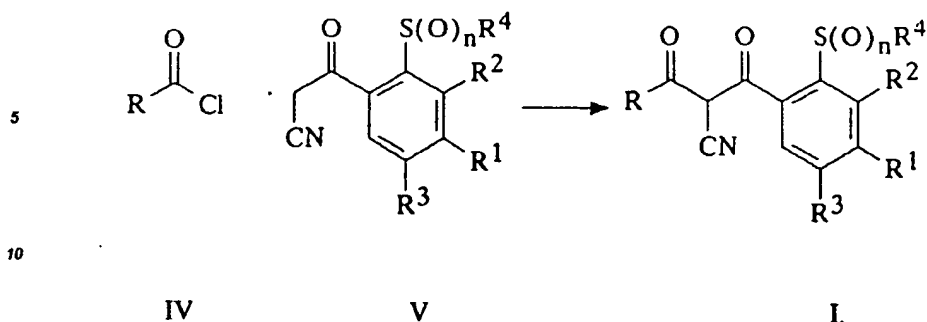
In the following description where symbols appearing in formulae are not specifically defined it is to be understood that they are 'as hereinbefore defined' in accordance with the first definition of each symbol in this specification.

It is to be understood that in the description of the following processes the sequences may be performed in different orders and that suitable protecting groups may be required to achieve the compounds sought.

According to a feature of the present invention the compounds of general formula I wherein n is 0 or 2 may be prepared by the reaction of a beta-ketonitrile of formula II with a benzoyl chloride of formula III in which n is 0 or 2 according to the following scheme:



According to a further feature of the present invention, compounds of general formula I wherein n is 0 or 2 may be prepared by the reaction of a beta-ketonitrile of formula V in which n is 0 or 2 with an acid chloride of formula IV according to the following scheme:



15

In general, these reactions occur advantageously in the presence of a base in a solvent or solvent mixture. Suitable bases include metal (e.g alkali metal or alkaline earth metal, preferably alkali metal) hydrides, hydroxides or alkoxides or salts such as sodium or lithium hydride, sodium hydroxide, potassium hydroxide, or magnesium ethoxide or magnesium methoxide, or potassium carbonate; and organic bases such as triethylamine.

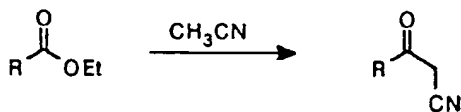
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Suitable solvents in which to conduct these reactions include ethers, such as tetrahydrofuran; hydrocarbons, such as toluene; or halogenated hydrocarbons, such as dichloromethane. These reactions can be conducted at a temperature between 0° C and the boiling point of the solvent.

25

Intermediates in the preparation of compounds of general formula I may be prepared by the application or adaptation of known methods. For instance, beta-ketonitriles of formula II may be prepared from acid chlorides of general formula IV by a number of methods well known in the chemical literature. For example, see Krauss, et al, *Synthesis*, 1983, 308, or Muth, et al, *J. Org. Chem.*, 1960, 25, 736. Alternatively, esters of general formula VI may be reacted with acetonitrile in accordance with Abramovitch and Hauser, *J. Am. Chem. Soc.*, 1942, 64, 2720, to provide beta-ketonitriles of formula II:

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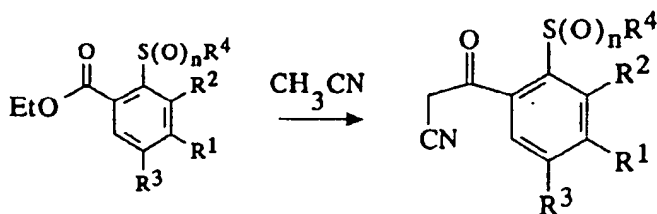
VI

II.

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The intermediate beta-ketonitriles of formula V in which n is 0 may be prepared from benzoyl chlorides of formula III in which n is 0 or from ethyl benzoates of general formula VII in which n is 0 in a manner analogous to the preparation of beta-ketonitriles of formula II set forth above:

45



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VII

V.

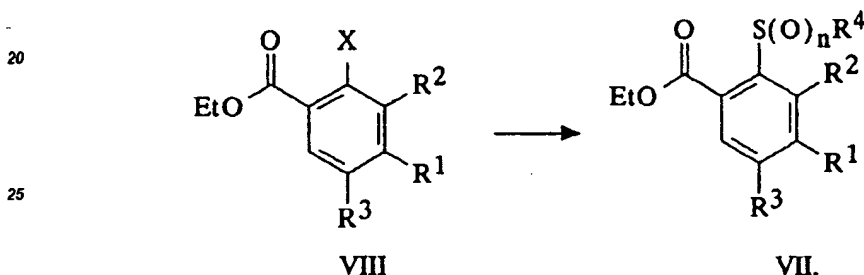
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Intermediate acid chlorides of general formula III or IV are generally known or can be prepared from carboxylic acids according to commonly accepted methods, for example by using thionyl chloride in chloroform at reflux.

Interconversion of compounds of general formula I or of intermediates is possible by the application or adaptation of known methods. Compounds in which n is 1 or 2 may be prepared by oxidation of the compounds in which n is 0 using, for example, 3-chloroperoxybenzoic acid in an inert solvent such as dichloromethane at a temperature between -30° C and the boiling point of the solvent.

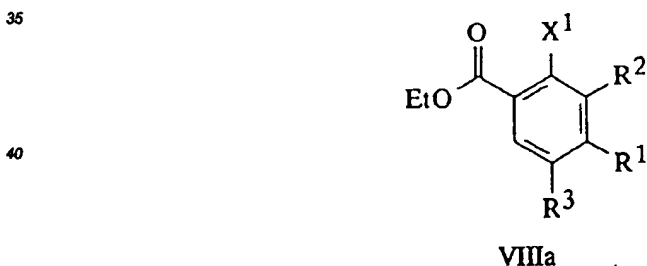
Compounds in which R¹, R² or R³ is a halogen atom may be prepared from compounds in which R¹, R², or R³ is replaced by an unsubstituted amino group by a Sandmeyer type reaction. This may be carried out using sodium nitrite in the presence of an acid such as hydrochloric acid or hydrobromic acid followed by treatment with for example copper (I) chloride or copper (I) bromide between room temperature and 80° C. Alternatively, diazotization may be carried out using an alkyl nitrite such as t-butyl nitrite in the presence of a halogenating agent such as copper (II) chloride or bromoform in an inert solvent such as acetonitrile.

Esters of general formula VII where n is 0 may be prepared by treatment of compounds of the general formula VIII in which X is a nitro group or a chlorine or bromine atom with an alkylmercaptan (i.e. R⁴SH) in the presence of a base in an inert solvent:



Suitable bases include sodium hydroxide and potassium carbonate, suitable inert solvents include dimethylformamide and dimethyl sulphoxide. The reaction may be conducted at a temperature between room temperature and 150°C.

Esters of general formula VII where n is 0 may also be prepared from compounds of general formula VIIIa:



45 in which X¹ is an unsubstituted amino group by the action of an alkyl nitrite such as tert-butylnitrite and a dialkyl disulfide in the presence of an inert solvent, for example chloroform at a temperature from ambient to the boiling point of the solvent.

Compounds in which R¹, R² or R³ is replaced by an unsubstituted amino group may be prepared by the reduction of compounds in which R¹, R² or R³ represents a nitro group, for example by means of tin (II) chloride and hydrochloric acid.

Compounds in which R¹, R² or R³ represents a cyano group may be prepared from compounds in which R¹, R² or R³ represents a group CO₂R⁵ via hydrolysis to the corresponding carboxylic acid, in which R⁵ is replaced by hydrogen, conversion to a corresponding acid halide, for example by treatment with thionyl chloride, treatment with ammonia to give the amide, and dehydration, for example by means of phosphorus oxychloride. Compounds in which R¹, R² or R³ represents a nitro group may be prepared by the oxidation of compounds in which R¹, R² or R³ is replaced by an unsubstituted amino group, for example by means of reaction with trifluoroperoacetic acid.

The following example illustrates the invention.

EXAMPLE 1

5 Preparation of 2-cyano-3-cyclopropyl-1-[2-(methylsulphonyl) phenyl] propan-1,3-dione, Compound A

Cyanoacetic acid (8.5 g) was dissolved in dry THF (250 ml), placed under an inert atmosphere and the solution was cooled using a dry ice-acetone bath. Butyl lithium (80 ml of a 2.5M solution in hexane) was added dropwise over 1 hour. During the addition the internal reaction temperature was maintained below -65° C. The reaction mixture was stirred in the dry ice-acetone bath for 1 hour, the cooling bath removed, and the reaction stirred for an additional hour during which time the internal temperature rose to 15° C. The resultant reaction mixture was cooled to -70° C and cyclopropanecarbonyl chloride (5.2 g) in THF (50 ml) added dropwise over 20 min. while keeping the temperature of the reaction mixture below -65° C. The reaction mixture was thus stirred for 1 hour, and then allowed to warm to room temperature overnight. The resultant mixture was acidified by the addition of 2N HCl (200 ml) and then diluted with CH₂Cl₂ (500 ml). The layers were separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were dried, altered; the solvents were removed to give 7.5g of an orange oil. The crude product was chromatographed on silica gel to afford 4.0g of 3-cyclopropyl-3-oxopropanonitrile as a pale orange oil, ¹H-nmr (CDCl₃): δ 0.9-1.3 (m, 4H), 1.9-2.1 (m, 1H), 3.66 (s, 2H).

To a mixture of absolute ethanol (7 ml) and CCl₄ (1 ml) under an inert atmosphere and at room temperature was added magnesium turnings (0.13g). The reaction mixture was stirred. To the reaction mixture was added 3-cyclopropyl-3-oxopropanonitrile (0.54g) in absolute ethanol (3 ml) and the resultant suspension progressively warmed during 30 minutes. The resultant yellow solution was evaporated to dryness. The solid was suspended in dry toluene (15 ml) and the resulting mixture warmed to 50° C. A solution of 2-(methylsulphonyl)-benzoyl chloride in dry toluene (5 ml) was added. The resultant reaction mixture was stirred at 50° C for 30 min., heated to reflux for 1 hour, cooled to room temperature, and allowed to sit overnight. To the reaction mixture was added 6N HCl (50 ml) and the two layers stirred vigorously until all the solid had dissolved. The layers were separated and the aqueous layer was extracted with ether. The organic extracts were combined with the organic layer and extracted with saturated NaHCO₃ solution. The basic extracts were acidified to pH 5 by the addition of concentrated HCl. The resulting mixture was extracted with ether. The ethereal extracts were combined washed with water, dried, filtered, and evaporated; 0.5g of a sticky red gum was obtained. This material was chromatographed on silica gel to afford 0.10g of 2-cyano-3-cyclopropyl-1-[2-(methylsulphonyl)phenyl]-propan-1,3-dione, Compound A, as a light orange solid, m.p. 155° C.

The compounds listed below may be prepared in manner similar to the method described above.

35 COMPOUND B:

1-[4-chloro-2-(methylsulphonyl)phenyl]-2-cyano-3-cyclopropylpropan-1,3-dione, m.p. 116° C, starting from 3-cyclopropyl-3-oxopropanonitrile and 4-chloro-2-(methylsulphonyl)benzoyl chloride.

40 COMPOUND C:

2-cyano-1-cyclopropyl-3-[2-(ethylsulphonyl)phenyl]propan-1,3-dione, m.p. 169° C, starting from 3-cyclopropyl-3-oxopropanonitrile and 2-(ethylsulphonyl)benzoyl chloride.

45 COMPOUND D:

2-cyano-1-cyclopropyl-3-[2-(1-methylethylsulphonyl)phenyl]propan-1,3-dione, m.p. 189° C, starting from 3-cyclopropyl-3-oxopropanonitrile and 2-(1-methylethylsulphonyl)benzoyl chloride.

50 COMPOUND E:

1-[4-chloro-2-(methylsulphonyl)phenyl]-2-cyano-3-(1-methylcyclopropyl)propan-1,3-dione, m.p. 122° C, starting from 3-(1-methylcyclopropyl)-3-oxopropanonitrile and 4-chloro-2-(methylsulphonyl)benzoyl chloride.

55 COMPOUND F:

1-[4-chloro-2-(methylsulphonyl)phenyl]-2-cyano-4-methylpentan-1,3-dione, m.p. 115.5° C, starting from 4-me-

thyl-3-oxopentanitrile and 4-chloro-2-(methylsulphonyl)benzoyl chloride.

COMPOUND G:

- 5 2-cyano-3-cyclopropyl-1-[4-methyl-2-(methylsulphonyl)phenyl]propan-1,3-dione, m.p. 129.5°C, starting from 3-cyclopropyl-3-oxopropanonitrile and 4-methyl-2-(methylsulphonyl)benzoyl chloride.

COMPOUND H:

- 10 2-cyano-3-cyclopropyl-1-[4-methoxy-2-(methylsulphonyl)phenyl]propan-1,3-dione, m.p. 151.5°C, starting from 3-cyclopropyl-3-oxopropanonitrile and 4-methoxy-2-(methylsulphonyl)benzoyl chloride.

COMPOUND I:

- 15 1-[4-chloro-2-(methylsulphenyl)phenyl]-2-cyano-3-cyclopropylpropan-1,3-dione, m.p. 154.5°C, starting from 3-cyclopropyl-3-oxopropanonitrile and 4-chloro-2-(methylsulphenyl)benzoyl chloride.

COMPOUND J:

- 20 1-[4-bromo-2-(methylsulphonyl)phenyl]-2-cyano-3-cyclopropylpropan-1,3-dione, m.p. 159°C, starting from 3-cyclopropyl-3-oxopropanonitrile and 4-bromo-2-(methylsulphonyl)benzoyl chloride.

COMPOUND K:

- 25 2-cyano-3-cyclopropyl-1-[2-(methylsulphonyl)-4-trifluoromethylphenyl]propan-1,3-dione, m.p. 107.5°C, starting from 3-cyclopropyl-3-oxopropanonitrile and 2-(methylsulphonyl)-4-trifluoromethylbenzoyl chloride.

The following examples illustrate the procedures for the preparation of intermediates relating to the present invention.

30 EXAMPLE 1(a)

Benzoyl chlorides are prepared by heating the appropriately substituted benzoic acids at reflux with thionyl chloride for 3 hours. The excess thionyl chloride is removed by evaporation and the benzoyl chlorides are used directly without further purification.

35

EXAMPLE 2(a)

- Potassium permanganate (316g) was added with stirring to a suspension of 4-bromo-2-(methylsulphenyl)toluene (90.5g) in water whilst maintaining the mixture at reflux. The mixture was stirred and heated at reflux for 3 hours. The mixture was filtered and the residue was washed with hot water. The filtrate was cooled to room temperature and extracted with ethyl acetate. The aqueous solution was acidified to pH 1, saturated with sodium chloride and extracted with ethyl acetate. The organic layer was washed with water, dried (anhydrous magnesium sulphate) and filtered. The filtrate was evaporated to dryness to give 4-bromo-2-(methylsulphenyl)benzoic acid (44.6g) as a light brown solid, m.p. 220-220.5°C.

- 45 By proceeding in a similar manner the following compounds were prepared from the appropriately substituted starting materials:

4-chloro-2-(methylsulphonyl)benzoic acid; NMR (CDCl₃ + DMSO-d₆):
3.34 (s, 3H), 7.5-7.8(m, 2H), 7.9 (s, 1H), 8.2-8.6 (bs, 1H).

50 EXAMPLE 3(a)

- Hydrogen peroxide (30%) was added to a cooled solution of 2-(methylsulphenyl)-4-trifluoromethylbenzoic acid (6.0g) and acetic anhydride (3.6ml) in acetic acid at 10°C. The mixture was allowed to warm slowly to room temperature and stirred for 0.5 hours. It was stirred and heated at 65°C for 3 hours. After cooling the mixture was poured into ice and extracted with ether. The organic layer was washed with water, aqueous ferrous sulphate solution, dried (anhydrous magnesium sulphate) and altered. The filtrate was evaporated to dryness to give 2-(methylsulphonyl)-4-trifluoromethylbenzoic acid (5.54g) as a white solid, m.p. 155.5-156.5°C.

EXAMPLE 4(a)

A solution of potassium peroxymonosulphate (23.8g) in water was added to a solution of 4-methyl-2-(methylsulphenyl)benzoic acid (4.7g) in methanol. The mixture was stirred for 5 hours and left to stand overnight at room temperature. The methanol was removed by evaporation and the resulting suspension was diluted with water and extracted with chloroform. The organic layer was dried (anhydrous magnesium sulphate) and altered. The filtrate was evaporated to dryness and the residue was triturated with a mixture of ether and cyclohexane to give 4-methyl-2-(methylsulphonyl)benzoic acid (4.4g) as a cream solid, m.p. 174-174.5°C.

By proceeding in a similar manner the following compound was prepared from the appropriately substituted starting material:

4-methoxy-2-(methylsulphonyl)benzoic acid, m.p. 180-80.5°C.

EXAMPLE 5(a)

n-Butyllithium (2.5M solution in hexane; 25 ml) was added under an inert atmosphere to a stirred solution of 4-bromo-3-(methylsulphenyl)benzotrifluoride (18.4g) in ether at whilst maintaining the temperature below -70°C. The mixture was stirred at -70°C for 2 hours and then poured onto solid carbon dioxide pellets. The mixture was stirred for 10 minutes and aqueous hydrochloric acid was added. The layers were separated and the aqueous layer was extracted with ether. The combined organic layers were washed with water, dried (anhydrous magnesium sulphate) and filtered. The filtrate was evaporated and the residue was triturated with cyclohexane and filtered to give 2-(methylsulphenyl)-4-trifluoromethylbenzoic acid (12.4g) as a white solid, NMR (CDCl₃) + DMSO-d₆: 2.45 (s,3H), 7.2(d,1H), 7.3(s,1H), 8.0(d,1H), 10.7-11.1(bs,1H).

By proceeding in a similar manner the following compound was prepared from the appropriately substituted starting material:

4-methyl-2-(methylsulphenyl)benzoic acid m.p. 178.5-179°C.

EXAMPLE 6(a)

t-Butyl nitrite (4ml) was added to a mixture of 5-chloro-2-methylaniline (4g) and dimethyl disulphide (26.3g) in chloroform. After the reaction started t-butyl nitrite (17.7ml) and 5-chloro-2-methylaniline (16g) were added simultaneously. The mixture was stirred at room temperature for 2 hours and left to stand overnight. The mixture was washed with water, aqueous hydrochloric acid (2M), water, dried (anhydrous magnesium sulphate) and filtered. The filtrate was evaporated to dryness to give 4-chloro-2-(methylsulphenyl)toluene (24.6g) as a red oil, NMR (CDCl₃): 2.2 (s,3H), 6.85 (s,2H), 7.0 (s,1H).

By proceeding in a similar manner the following compounds were prepared from the appropriately substituted starting materials:

4-bromo-3-(methylsulphenyl)benzotrifluoride, b.p. 84-88°C at 2mm Hg;

4-bromo-3-(methylsulphenyl)toluene, b.p. 118-124°C at 7mm Hg;

EXAMPLE 7(a)

A cooled solution of sodium nitrite (5.8g) in concentrated sulphuric acid (50ml) was added dropwise to a stirred solution of 4-methyl-3-(methylsulphenyl)aniline (12.8g) in glacial acetic acid at 20°C. The resulting suspension was added to a mixture of copper (I) bromide (12g), aqueous hydrobromic acid (48.50%) and ice. The mixture was stirred at room temperature for 3 hours then diluted with water and extracted with ethyl acetate. The organic layer was washed with water, aqueous sodium hydroxide (2M), dried (anhydrous magnesium sulphate) and filtered. The filtrate was evaporated to dryness. The residue was triturated with hot cyclohexane and filtered. The filtrate was evaporated to dryness to give 4-bromo-2-(methylsulphenyl)toluene (8.6g) as a brown oil, NMR (CDCl₃): 2.15(s,3H), 2.2(s,3H), 6.5-7.1 (m,3H).

EXAMPLE 8(a)

Concentrated hydrochloric acid (128 ml) was added slowly to a suspension of 2-(methylsulphenyl)-4-nitrotoluene (36.6g) in methanol. Iron powder (36g) was added with stirring whilst maintaining the temperature below 50°C. The mixture was stirred at room temperature for 4 hours. The mixture was poured into water neutralized (by the addition of sodium carbonate), filtered and the residue was extracted with dichloromethane. The aqueous layer was extracted with dichloromethane and the combined organic layers were washed with aqueous sodium chloride solution, dried (anhydrous magnesium sulphate) and filtered. The filtrate was evapo-

rated to dryness and the residue was purified by column chromatography on silica eluted with a mixture of ethyl acetate and n-hexane to give 4-methyl-3-(methylsulphenyl)aniline (12.8g) as an orange solid, NMR (CDCl₃) 2.2(s,3H), 2.35(s,3H), 3.45(s,2H), 6.1-6.9(m,3H).

According to a feature of the present invention, there is provided a method for controlling the growth of weeds (i.e. undesired vegetation) at a locus which comprises applying to the locus a herbicidally effective amount of at least one 2-cyano-1,3-dione derivative of general formula (I) or an agriculturally acceptable salt thereof. For this purpose, the 2-cyano-1,3-dione derivatives are normally used in the form of herbicidal compositions (i.e. in association with compatible diluents or carriers and/or surface active agents suitable for use in herbicidal compositions), for example as hereinafter described.

The compounds of general formula (I) show herbicidal activity against dicotyledonous (i.e. broad-leaved) and monocotyledonous (e.g. grass) weeds by pre- and/or, post-emergence application.

By the term "pre-emergence application" is meant application to the soil in which the weed seeds or seedlings are present before emergence of the weeds above the surface of the soil. By the term "post-emergence application" is meant application to the aerial or exposed portions of the weeds which have emerged above the surface of the soil. For example, the compounds of general formula (I) may be used to control the growth of

* broad-leaved weeds, for example, *Abutilon theophrasti*, *Amaranthus retroflexus*, *Bidens pilosa*, *Chenopodium album*, *Galium aparine*, *Ipomoea* spp. e.g. *Ipomoea purpurea*, *Sesbania exaltata*, *Sinapis arvensis*, *Solanum nigrum* and *Xanthium strumarium*, and

* grass weeds, for example *Alopecurus myosuroides*, *Avena fatua*, *Digitaria sanguinalis*, *Echinochloa crus-galli*, *Eleusine indica* and *Setaria* spp. e.g. *Setaria faberii* or *Setaria viridis*, and

* sedges, for example, *Cyperus esculentus*.

The amounts of compounds of general formula (I) applied vary with the nature of the weeds, the compositions used, the time of application, the climatic and edaphic conditions and (when used to control the growth of weeds in crop-growing areas) the nature of the crops. When applied to a crop-growing area, the rate of application should be sufficient to control the growth of weeds without causing substantial permanent damage to the crop. In general, taking these factors into account, application rates between 0.01 kg and 5 kg of active material per hectare give good results. However, it is to be understood that higher or lower application rates may be used, depending upon the particular problem of weed control encountered.

The compounds of general formula (I) may be used to control selectively the growth of weeds, for example to control the growth of those species hereinbefore mentioned, by pre- or post-emergence application in a directional or non-directional fashion, e.g. by directional or non-directional spraying, to a locus of weed infestation which is an area used, or to be used, for growing crops, for example cereals, e.g. wheat, barley, oats, maize and rice, soya beans, field and dwarf beans, peas, lucerne, cotton, peanuts, flax, onions, carrots, cabbage, oilseed rape, sunflower, sugar beet, and permanent or sown grassland before or after sowing of the crop or before or after emergence of the crop. For the selective control of weeds at a locus of weed infestation which is an area used, or to be used, for growing of crops, e.g. the crops hereinbefore mentioned, application rates between 0.01 kg and 4.0 kg, and preferably between 0.01 kg and 2 kg, of active material per hectare are particularly suitable.

The compounds of general formula (I) may also be used to control the growth of weeds, especially those indicated above, by pre- or post-emergence application in established orchards and other tree-growing areas, for example forests, woods and parks, and plantations, e.g. sugar cane, oil palm and rubber plantations. For this purpose they may be applied in a directional or non-directional fashion (e.g. by directional or non-directional spraying) to the weeds or to the soil in which they are expected to appear, before or after planting of the trees or plantations at application rates between 0.25 kg and 5 kg, and preferably between 0.5 kg and 4 kg of active material per hectare.

The compounds of general formula (I) may also be used to control the growth of weeds, especially those indicated above, at loci which are not crop-growing areas but in which the control of weeds is nevertheless desirable.

Examples of such non-crop-growing areas include airfields, industrial sites, railways, roadside verges, the verges of rivers, irrigation and other waterways, scrublands and fallow or uncultivated land, in particular where it is desired to control the growth of weeds in order to reduce fire risks. When used for such purposes in which a total herbicidal effect is frequently desired, the active compounds are normally applied at dosage rates higher than those used in crop-growing areas as hereinbefore described. The precise dosage will depend upon the nature of the vegetation treated and the effect sought.

Pre- or post-emergence application, and preferably pre-emergence application, in a directional or non-directional fashion (e.g. by directional or non-directional spraying) at application rates between 1 kg and 20 kg,

and preferably between 5 and 10 kg, of active material per hectare are particularly suitable for this purpose.

When used to control the growth of weeds by pre-emergence application, the compounds of general formula (I) may be incorporated into the soil in which the weeds are expected to emerge. It will be appreciated that when the compounds of general formula (I) are used to control the growth of weeds by post-emergence application, i.e. by application to the aerial or exposed portions of emerged weeds, the compounds of general formula (I) will also normally come into contact with the soil and may also then exercise a pre-emergence control on later-germinating weeds in the soil.

Where especially prolonged weed control is required, the application of the compounds of general formula (I) may be repeated if required.

According to a further feature of the present invention, there are provided compositions suitable for herbicidal use comprising one or more of the 2-cyano-1,3-dione derivatives of general formula (I) or an agriculturally acceptable salt thereof in association with, and preferably homogeneously dispersed in, one or more compatible herbicidally- acceptable diluents or carriers and/or surface active agents [i.e. diluents or carriers and/or surface active agents of the type generally accepted in the art as being suitable for use in herbicidal compositions and which are compatible with compounds of general formula (I)]. The term "homogeneously dispersed" is used to include compositions in which the compounds of general formula (I) are dissolved in other components. The term "herbicidal compositions" is used in a broad sense to include not only compositions which are ready for use as herbicides but also concentrates which must be diluted before use. Preferably, the compositions contain from 0.05 to 90% by weight of one or more compounds of general formula (I).

The herbicidal compositions may contain both a diluent or carrier and surface-active (e.g. wetting, dispersing, or emulsifying) agent. Surface-active agents which may be present in herbicidal compositions of the present invention may be of the ionic or non-ionic types, for example sulphuric acid esters, quaternary ammonium derivatives, products based on condensates of ethylene oxide with alkyl and polyaryl phenols, e.g. nonyl- or octyl-phenols, or carboxylic acid esters of anhydrosorbitols which have been rendered soluble by etherification of the free hydroxy groups by condensation with ethylene oxide, alkali and alkaline earth metal salts of sulphuric acid esters and sulphonic acids such as dinonyl- and dioctyl-sodium sulphonosuccinates and alkali and alkaline earth metal salts of high molecular weight sulphonic acid derivatives such as sodium and calcium lignosulphonates and sodium and calcium alkylbenzene sulphonates.

Suitably, the herbicidal compositions according to the present invention may comprise up to 10% by weight, e.g. from 0.05% to 10% by weight, of surface-active agent but, if desired, herbicidal compositions according to the present invention may comprise higher proportions of surface-active agent, for example up to 15% by weight in liquid emulsifiable suspension concentrates and up to 25% by weight in liquid water soluble concentrates.

Examples of suitable solid diluents or carriers are aluminium silicate, talc, calcined magnesite, kieselguhr, tricalcium phosphate, powdered cork adsorbent carbon black and clays such as kaolin and bentonite. The solid compositions (which may take the form of dusts, granules or wettable powders) are preferably prepared by grinding the compounds of general formula (I) with solid diluents or by impregnating the solid diluents or carriers with solutions of the compounds of general formula (I) in volatile solvents, evaporating the solvents and, if necessary, grinding the products so as to obtain powders. Granular formulations may be prepared by absorbing the compounds of general formula (I) (dissolved in suitable solvents, which may, if desired, be volatile) onto the solid diluents or carriers in granular form and, if desired, evaporating the solvents, or by granulating compositions in powder form obtained as described above. Solid herbicidal compositions, particularly wettable powders and granules, may contain wetting or dispersing agents (for example of the types described above), which may also, when solid, serve as diluents or carriers.

Liquid compositions according to the invention may take the form of aqueous, organic or aqueous-organic solutions, suspensions and emulsions which may incorporate a surface-active agent. Suitable liquid diluents for incorporation in the liquid compositions include water, glycols, tetrahydrofurfuryl alcohol, acetophenone, cyclohexanone, isophorone, toluene, xylene, mineral, animal and vegetable oils and light aromatic and naphthenic fractions of petroleum (and mixtures of these diluents). Surface-active agents, which may be present in the liquid compositions, may be ionic or non-ionic (for example of the types described above) and may, when liquid, also serve as diluents or carriers.

Powders, dispersible granules and liquid compositions in the form of concentrates may be diluted with water or other suitable diluents, for example mineral or vegetable oils, particularly in the case of liquid concentrates in which the diluent or carrier is an oil, to give compositions ready for use.

When desired, liquid compositions of the compound of general formula (I) may be used in the form of self-emulsifying concentrates containing the active substances dissolved in the emulsifying agents or in solvents containing emulsifying agents compatible with the active substances, the simple addition of water to such concentrates producing compositions ready for use.

Liquid concentrates in which the diluent or carrier is an oil may be used without further dilution using the electrostatic spray technique.

Herbicidal compositions according to the present invention may also contain, if desired, conventional adjuvants such as adhesives, protective colloids, thickeners, penetrating agents, stabilisers, sequestering agents, anti-caking agents, colouring agents and corrosion inhibitors. These adjuvants may also serve as carriers or diluents.

Unless otherwise specified, the following percentages are by weight. Preferred herbicidal compositions according to the present invention are

- * aqueous suspension concentrates which comprise from 10 to 70% of one or more compounds of general formula (I), from 2 to 10% of surface-active agent, from 0.1 to 5 % of thickener and from 15 to 87.9 % of water,
- * wettable powders which comprise from 10 to 90% of one or more compounds of general formula (I), from 2 to 10% of surface-active agent and from 8 to 88% of solid diluent or carrier,
- * soluble powders which comprise from 10 to 90% of one or more compounds of general formula (I), from 2 to 40% of sodium carbonate and from 0 to 88% of solid diluent
- * liquid water soluble concentrates which comprise from 5 to 50%, e.g. 10 to 30%, of one or more compounds of general formula (I), from 5 to 25% of surface-active agent and from 25 to 90%, e.g. 45 to 85%, of water miscible solvent, e.g. dimethylformamide, or a mixture of water-miscible solvent and water,
- * liquid emulsifiable suspension concentrates which comprise from 10 to 70% of one or more compounds of general formula (I), from 5 to 15% of surface-active agent, from 0.1 to 5% of thickener and from 10 to 84.9% of organic solvent
- * granules which comprise from 1 to 90%, e.g. 2 to 10% of one or more compounds of general formula (I), from 0.5 to 7%, e.g. 0.5 to 2%, of surface-active agent and from 3 to 98.5%, e.g. 88 to 97.5%, of granular carrier and,
- * emulsifiable concentrates which comprise 0.05 to 90%, and preferably from 1 to 60% of one or more compounds of general formula (I), from 0.01 to 10%, and preferably from 1 to 10%, of surface-active agent and from 9.99 to 99.94%, and preferably from 39 to 98.99%, of organic solvent.

Herbicidal compositions according to the present invention may also comprise the compounds of general formula (I) in association with, and preferably homogeneously dispersed in, one or more other pesticidally active compounds and, if desired, one or more compatible pesticidally acceptable diluents or carriers, surface-active agents and conventional adjuvants as hereinbefore described. Examples of other pesticidally active compounds which may be included in, or used in conjunction with, the herbicidal compositions of the present invention include herbicides, for example to increase the range of weed species controlled for example alachlor [2-chloro-2,6'-diethyl-N-(methoxy-methyl)-acetanilide], atrazine [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine], bromoxynil [3,5-dibromo-4-hydroxybenzonitrile], chlortoluron [N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea], cyanazine [2-chloro-4-(1-cyano-1-methylethylamino)-6-ethylamino-1,3,5-triazine], 2,4-D [2,4-dichlorophenoxy-acetic acid], dicamba [3,6-dichloro-2-methoxybenzoic acid], difenzoquat [1,2-dimethyl-3,5-diphenyl-pyrazolium salts], flumetroluron [methyl N-2-(N-benzoyl-3-chloro-4-fluoroanilino)-propionate], fluometuron [N'-(3-trifluoro-methylphenyl)-N,N-dimethylurea], isoproturon [N'-(4-isopropylphenyl)-N,N-dimethylurea], nicosulfuron [2-(4,6-dimethoxypyrimidin-2-ylcarbonylsulfamoyl)-N,N-dimethylnicotinamide] insecticides, e.g. synthetic pyrethroids, e.g. permethrin and cypermethrin, and fungicides, e.g. carbamates, e.g. methyl N-(1-butyl-carbamoylbenzimidazol-2-yl)carbamate, and triazoles e.g. 1-(4-chloro-phenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-butan-2-one.

Pesticidally active compounds and other biologically active materials which may be included in, or used in conjunction with, the herbicidal compositions of the present invention, for example those hereinbefore mentioned, and which are acids, may, if desired, be utilized in the form of conventional derivatives, for example alkali metal and amine salts and esters.

According to a further feature of the present invention there is provided an article of manufacture comprising at least one of the 2-cyano-1,3-dione derivatives of general formula (I) or an agriculturally acceptable salt thereof or, as is preferred, a herbicidal composition as hereinbefore described, and preferably a herbicidal concentrate which must be diluted before use, comprising at least one of the 2-cyano-1,3-dione derivatives of general formula (I) within a container for the aforesaid derivative or derivatives of general formula (I), or a said herbicidal composition, and instructions physically associated with the aforesaid container setting out the manner in which the aforesaid derivative or derivatives of general formula (I) or herbicidal composition contained therein is to be used to control the growth of weeds. The containers will normally be of the types conventionally used for the storage of chemical substances which are solid at normal ambient temperatures and herbicidal compositions particularly in the form of concentrates, for example cans and drums of metal, which may be internally lacquered, and plastics materials, bottles or glass and plastics materials and, when the contents of the

container is a solid, for example granular, herbicidal compositions, boxes, for example of cardboard, plastics materials and metal, or sacks. The containers will normally be of sufficient capacity to contain amounts of the 2-cyano-1,3-dione derivative or herbicidal compositions sufficient to treat at least one acre of ground to control the growth of weeds therein but will not exceed a size which is convenient for conventional methods of handling.

5 The instructions will be physically associated with the container, for example by being printed directly thereon or on a label or tag affixed thereto. The directions will normally indicate that the contents of the container, after dilution if necessary, are to be applied to control the growth of weeds at rates of application between 0.01 kg and 20 kg of active material per hectare in the manner and for the purposes hereinbefore described.

The following Examples illustrate herbicidal compositions according to the present invention:

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EXAMPLE C1

A wettable powder was formed from:

- * active ingredient (compound A): 50% w/w
 - 15 * nonylphenol/ethylene oxide condensate containing 9 moles of ethylene oxide per mol of phenol: 5% w/w
 - * silicon dioxide of micro-fine particle size: 5% w/w
 - * synthetic magnesium silicate carrier: 40% w/w
- by absorbing the condensate on the silicon dioxide, mixing with the other ingredients and grinding the mixture in a hammermill to give a wettable powder.

20 Similar wettable powders may be prepared as described above by replacing the 2-cyano-1,3-dione (compound A) by other compounds of general formula (I).

EXAMPLE C2

25 An aqueous suspension concentrate was formed from

- * active ingredient (compound A): 50% w/v
- * nonylphenol/ethylene oxide condensate containing 9 moles of ethylene oxide per mol of phenol: 1 % w/v
- * sodium salt of polycarboxylic acid: 0.2% w/v
- * Ethylene glycol : 5% w/v
- 30 * polysaccharide xanthan gum thickener: 0.15% w/v
- * water to 100% by volume

by intimately mixing the ingredients and grinding in a ball-mill for 24 hours.

Similar aqueous concentrates may be prepared as described above by replacing the 2-cyano-1,3-dione (compound A) by other compounds of general formula (I).

35 Representative compounds of general formula (I) have been used in herbicidal applications according to the following procedures.

Method of use of herbicidal compounds:40 Herbicidal activity:

Appropriate quantities of the compounds used to treat the plant were dissolved in acetone to give solutions equivalent to an application rate of up to 4000g of the compounds used to treat the plants per hectare (g/ha). These solutions were applied at 260 litres of spray fluid per hectare.

45

a) Pre-emergence application weed control.

Seeds (weeds or crops) were sown in loam soil pots.

The compounds of the invention were applied to the soil surface as described above.

50

b) Post-emergence application weed control.

Weed species were grown until ready for spraying with the compounds of the invention. The growth stage of the plants at spraying were as follows :

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1) Broad-leaved weeds:

Abutilon theophrasti:	1-2 leaves.
Amaranthus retroflexus:	1-2 leaves.
Galium aparine:	1-2 whorls.

	Sinapis arvensis:	2 leaves.
	Ipomoea purpurea:	1-2 leaves.
	Xanthium strumarium:	2 leaves.
	2) Grass weeds:	
5	Alopecurus myosuroides:	2 leaves.
	Avena fatua:	1-2 leaves.
	Echinochloa crus-galli	2-3 leaves.
	Setaria viridis:	2-3 leaves.
	3) Sedges:	
10	Cyperus esculentus:	3 leaves.

c) Crop tolerance

Compounds of the invention were applied pre-emergence as in (a) or post emergence (3-leaf stage) to the following crops:- wheat, maize, rice, soya and cotton.

A single pot of each plant species was allocated to each treatment with unsprayed controls and controls sprayed with acetone alone.

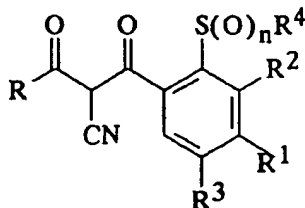
After treatment, the pots were kept in the greenhouse and were watered overhead.

Visual assessment of phytotoxicity was made 17-20 days after spraying. Weed control results were expressed as the percentage reduction in growth or kill of the weeds, in comparison with the plants in the control pots. Crop tolerance was expressed as the percentage damage to crop.

Representative compounds of the invention, when used at an application rate of 4kg/ha or less, show herbicidal activity against one or more of the weed species listed above: such compounds also show selectivity on one or more of the listed crop species.

Claims

1. A 2-cyano-1,3-dione derivative of formula I:



I

wherein

- 45 R represents:-
a straight- or branched-chain alkyl group containing up to 6 carbon atoms which is optionally substituted by one or more halogen atoms which may be the same or different; or
a cycloalkyl group containing from 3 to 6 carbon atoms which is optionally substituted by one or more groups selected from R⁵ and one or more halogen atoms which may be the same or different,
- 50 R¹ represents:-
a halogen atom or hydrogen atom, or
a straight- or branched-chain alkyl group containing up to 6 carbon atoms which is substituted by -OR⁵; or
a group selected from R⁵, nitro, cyano, SR⁵, -OR⁵, -O(CH₂)_mOR⁵, or -CO₂R⁵.
- 55 R² and R³, which may be the same or different, each represents:-
a halogen or hydrogen atom, or
a straight- or branched-chain alkyl group containing up to 6 carbon atoms which is substituted by -OR⁵; or

a group selected from R⁵, nitro, cyano, -OR⁵, -O(CH₂)_mOR⁵, or -CO₂R⁵;
 provided that at least one of R² and R³ is hydrogen,
 R⁴ and R⁵, which may be the same or different, each represent:-
 a straight- or branched-chain alkyl group containing up to 6 carbon atoms which is optionally sub-
 5 stituted by one or more halogen atoms which may be the same or different,
 m is an integer from 1 to 3, and
 n is zero, 1 or 2;
 with the proviso that when n is zero, R¹ does not represent -SR⁵;
 an enolic tautomeric form thereof,
 10 or an agriculturally acceptable salt of the enolic tautomeric form.

2. A compound according to claim 1 wherein:

- (a) R¹ represent:-
 a halogen atom or hydrogen atom, or
 15 a group selected from
 -OR⁵, or R⁵, or nitro;
 and/or
 (b) R² and R³, which may be the same or different, each represents:-
 a halogen atom or hydrogen atom,
 20 a straight- or branched-chain alkyl group containing up to 6 carbon atoms which is substituted
 by -OR⁵; or
 a group selected from
 R⁵ -OR⁵ -O(CH₂)_mOR⁵ where m is 2 or 3, or -CO₂R⁵;
 provided that at least one of R² and R³ is hydrogen;
 25 and/or
 (c) R⁴ represents:-
 a straight- or branched-chain alkyl group containing up to 4 carbon atoms which is optionally sub-
 stituted by one or more halogen atoms which may be the same or different;
 and/or
 30 (d) R⁵ represents:
 a straight- or branched-chain alkyl group containing up to 4 carbon atoms which is optionally sub-
 stituted by one or more halogen atoms, which may be the same or different;
 and
 (e) 'halogen' means chlorine, bromine or fluorine.

3. A compound according to claim 1 or 2 wherein

- (a) R represents:-
 methyl, isopropyl, t-butyl, cyclopropyl or 1-methylcyclopropyl;
 and/or
 40 (b) R¹ represents:-
 a halogen atom or hydrogen atom, or
 a group selected from methoxy, ethoxy, trifluoromethoxy, methyl, trifluoromethyl or nitro;
 and/or
 (c) R² and R³, which may be the same or different, each represents:-
 45 a halogen atom or hydrogen atom, or methoxymethyl, methyl, trifluoromethyl, methoxy, ethoxy,
 isopropoxy, 2-ethoxyethoxy, 2-methoxyethoxy, carbomethoxy, carboethoxy or carboisopropoxy;
 and/or
 (d) R⁴ represents isopropyl, methyl or ethyl;
 and/or
 50 (e) R⁵ represents:
 methyl, ethyl, isopropyl, or trifluoromethyl.

4. A compound according to claim 1, 2 or 3 in which R³ represents a hydrogen atom.

55 5. A compound according to any one of claims 1 to 4 wherein:

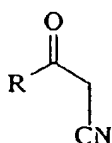
R represents isopropyl, cyclopropyl or 1-methylcyclopropyl;
 R¹ represents hydrogen, chlorine, bromine, trifluoromethyl, methoxy or methyl;
 R² and R³ each represent hydrogen;

R⁴ represents methyl, ethyl or isopropyl; and
n is zero, 1 or 2.

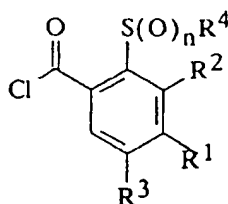
6. A compound according to claim 1 which is

2-cyano-3-cyclopropyl-1-[2-(methylsulphonyl)phenyl]propan-1,3-dione,
1-[4-chloro-2-(methylsulphonyl)phenyl]-2-cyano-3-cyclopropylpropan-1,3-dione,
2-cyano-1-cyclopropyl-3-[2-(ethylsulphonyl)phenyl]propan-1,3-dione,
2-cyano-1-cyclopropyl-3-[2-(1-methylethylsulphonyl)phenyl]propan-1,3-dione,
1-[4-chloro-2-(methylsulphonyl)phenyl]-2-cyano-3-(1-methylcyclopropyl)propan-1,3-dione,
1-[4-chloro-2-(methylsulphonyl)phenyl]-2-cyano-4-methylpentan-1,3-dione,
2-cyano-3-cyclopropyl-1-[4-methyl-2-(methylsulphonyl)phenyl]propan-1,3-dione,
2-cyano-3-cyclopropyl-1-[4-methoxy-2-(methylsulphonyl)phenyl]propan-1,3-dione,
1-[4-chloro-2-(methylsulphonyl)phenyl]-2-cyano-3-cyclopropylpropan-1,3-dione,
1-[4-bromo-2-(methylsulphonyl)phenyl]-2-cyano-3-cyclopropylpropan-1,3-dione, or
2-cyano-3-cyclopropyl-1-[2-(methylsulphonyl)-4-trifluoromethylphenyl]propan-1,3-dione,
or an agriculturally acceptable salt thereof.

7. A process for the preparation of a compound of general formula (I) according to claim 1 which comprises:
a) the reaction of a beta-ketonitrile of formula II with a benzoyl chloride of formula III:



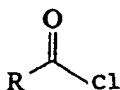
II



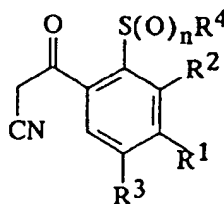
III

wherein R, R¹, R², R³ and R⁴ are defined in claim 1 and n is 0 or 2;

- b) the reaction of an acid chloride of formula IV with a beta-ketonitrile of formula V:



IV



V

wherein R, R¹, R², R³ and R⁴ are as defined in claim 1 and n is 0 or 2; or

- c) optionally oxidising a compound of formula I wherein n is 0 to a compound wherein n is 1 or 2;
and optionally converting a 2-cyano-1,3-dione thus obtained to a salt thereof.

8. A process according to claim 7 wherein the reaction is carried out in the presence of a base in a solvent or solvent mixture at a temperature from 0°C to the boiling point of the solvent.
9. A herbicidal composition which comprises as an active ingredient a herbicidally effective amount of a 2-cyano-1,3-dione derivative of general formula I or an agriculturally acceptable salt thereof according to any one of claims 1 to 6 in association with a herbicidally acceptable diluent or carrier, and optionally one or more surface active agents.

10. A herbicidal composition according to claim 9 which comprises from 0.05 to 90% by weight of active ingredient.
- 5 11. A herbicidal composition according to claim 9 or 10 which comprises from 0.05% to 25% by weight of surface active agent, and optionally an adhesive, protective colloid, thickener, penetrating agent, stabiliser, sequestering agent, anti-caking agent, colouring agent and/or corrosion inhibitor.
- 10 12. A herbicidal composition according to claim 9, 10 or 11 which is in the form of an aqueous suspension concentrate, a wettable powder, a soluble powder, a liquid water soluble concentrate, a liquid emulsifiable suspension concentrate, granules, or an emulsifiable concentrate.
- 15 13. A method of controlling the growth of weeds at a locus which comprises applying thereto a 2-cyano-1,3-dione derivative of general formula I according to any one of claims 1 to 6 or an agriculturally acceptable salt thereof.
- 20 14. A method according to claim 13 wherein the locus is an area used, or to be used, for the growing of crops, using an application rate of between 0.01 kg and 4.0 kg of active material per hectare.
- 25 15. A method according to claim 13 wherein the locus is not a crop growing area, using an application rate between 1 kg and 20 kg of active material per hectare.
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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 0608

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 374 811 (BASF) ---		C07C317/44 C07C317/46 C07C323/62 A01M41/10
A	EP-A-0 398 692 (SHIONOGI) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C07C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 03 APRIL 1992	Examiner ZAROKOSTAS K.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : number of the same patent family, corresponding document</p>			

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